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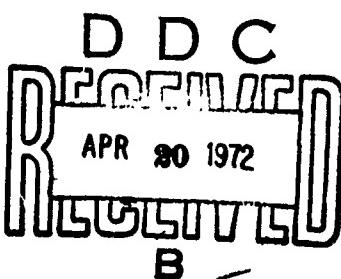
**X-RAY DIFFRACTION STUDIES OF THE ROLE  
OF HYDROGEN BONDING IN THE  
LOW TEMPERATURE BEHAVIOR OF MATERIALS**

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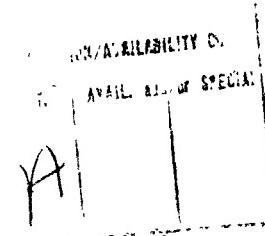
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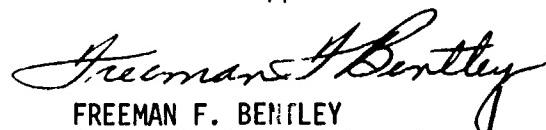
## FOREWORD

This report was prepared jointly by the University of Dayton Research Institute and the Air Force Materials Laboratory. Work performed by the Air Force Materials Laboratory was performed under Project No. 7360, "Chemical, Physical and Thermodynamic Properties of Aircraft, Missile and Spacecraft Materials", and Task No. 736005, "Compositional, Atomic and Molecular Analysis of Experimental Materials for Advanced Air Force Systems". The portion of the work performed by the University of Dayton Research Institute was performed under United States Air Force Contract No. F33615-69-C-1330 (Project 7360; Task 736001 and 736005) with Mr. Hyman Marcus, AFML/LPT, as the contract monitor. Capt. H. A. Wells, Materials Physics Division, LPA, was the technical project engineer.

The report covers work performed inhouse, by the authors, during November and December 1970. The manuscript was released for publication by the authors in October 1971.

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This technical report has been reviewed and is approved.



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## ABSTRACT

X-Ray Diffraction strip chart recordings were obtained at 100°K and 300°K for powder samples of urea and seven carbohydrates. A combination of known crystallographic data and a least squares fit program revealed the temperature dependence of the unit cell for urea and three of the carbohydrates. In all cases, a contraction on cooling was observed.

While the volume of data produced did not justify any positive conclusions, the results did not contradict the model of Sklar et al. assigning the entire shrinkage to hydrogen bond contraction. The model remains valid for interpretation of infrared data, at least until further x-ray data becomes available.

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## I. INTRODUCTION

In recent years, low temperature infrared and Raman spectroscopy have been shown to be very sensitive tools for characterization of solid structures (Ref 1). These tools are even more sensitive when the structures in question have network hydrogen bonding (Refs 2, 3). Interpretation, however, has not kept pace with the volume of new data being produced. One of the principle reasons for this lag is a lack of x-ray structural data at non-ambient temperatures for purposes of comparison with spectral results for model systems. A complete structural solution for a series of compounds at a series of temperatures is a rather formidable task at present. However, a first approximation to this information, the temperature dependence of the unit cell parameters, is in principle quicker and easier to obtain.

A series of compounds including urea and seven carbohydrates were selected for study. Urea was a calibration compound, since the temperature dependence of its structure is already in the literature (Ref 4). The other compounds were chosen from the carbohydrates because of the uniquely high level of solid state hydrogen bonding present in this class. All compounds chosen were readily available in pure, highly crystalline form. In addition, only compounds whose room temperature crystal structures and room and low temperature vibrational spectra were known were chosen.

The ultimate goal of this study was to correlate temperature dependent changes in vibrational spectra with structural changes found by x-ray diffraction and thus to gain an understanding of the role of hydrogen bonding in determining the temperature dependence of materials' properties. This report discusses the x-ray portion of the study, with further discussions to be the subject of a future report.

## II. MATERIALS AND APPARATUS

Commercial samples of urea,  $\alpha$ -D-glucose,  $\beta$ -D-glucose, raffinose (hydrate),  $\alpha$ -n-acetyl-D-glucosamine,  $\beta$ -maltose,  $\beta$ -cellobiose,  $\beta$ -arabinose, and sucrose were prepared by grinding about 50 mg in a boron carbide mortar and adding approximately five drops of paraffin oil to form a paste-like material. The paste was smeared onto a copper specimen mount which was attached to a cold finger extending from a dewar. The specimen mount was housed in an evacuable chamber equipped with beryllium windows. Low-temperatures were achieved through conduction by adding appropriate coolants (e.g., liquid nitrogen, dry ice and acetone, ice and water, etc.).

A Siemens generator and diffractometer equipped with a nickel-filtered copper x-ray source were employed in conjunction with a Hamner scintillation counter, Hamner electronics, and a Brown recorder. The  $2\theta$  drive was fixed at  $0.5^\circ/\text{min}$ . with chart speed of 0.5 in./min.

Diffraction spectra were obtained for each specimen at room temperature and at liquid nitrogen temperature under reduced pressure (approximately  $100 \mu$ ). The specimen mount was warmed to room temperature, and the entire experiment was repeated. The average of the two runs was then used as input for a least squares unit cell parameter refinement program. The overall standard deviation was demonstrated to be  $0.01^\circ 2\theta$ .

Angular calibration was achieved by observing the copper diffraction spectrum throughout the range  $40^\circ$  to  $75^\circ 2\theta$  and measuring the deviation from ASTM card # 4-0836. Temperature calibration was accomplished by comparing diffraction data with that of Skiar et al. (Ref 4). Specimen temperatures of  $-190^\circ \pm 5^\circ\text{C}$  are estimated (previous unpublished results showed specimen temperature of  $-191^\circ\text{C}$  as measured with an iron-constantan thermocouple connected to a Leeds and Northrup potentiometer).

### III. RESULTS

Tables I through IX list diffraction data obtained from the sugars investigated in this work. Good reproducibility of data was achieved in all cases, but a discrepancy exists between our data and that calculated from unit cell parameters in the literature (Refs 8, 9, 10, 11, 12) for the compounds  $\alpha$ -D-glucose,  $\beta$ -D-glucose, raffinose, maltose and  $\beta$ -arabinose. Both the excellent precision ( $\pm 0.01^\circ 2\theta$ ) attained in this investigation and the good agreement of our diffraction data with that calculated from the literature for urea, sucrose,  $\beta$ -cellobiose, and  $\alpha$ -n-acetyl-glucosamine, makes experimental error very improbable. The infrared spectra of most of the materials used in this investigation agreed with spectra previously published in the literature (Refs 13, 14, 15). We cannot, therefore, explain this mysterious source of discrepancy or where it originates.

A least squares refinement program provided the data listed in table X. Table XI provides data for unit cell parameters at room temperature as reported in the literature. All of the data in table X is within a standard deviation range of  $\pm 0.01\text{\AA}$  for the cell length and  $\pm 0.5^\circ$  for the axial angle  $\beta$ . All refinements converged within five cycles reaching a minimum  $2\theta$  tolerance of 0.04 and a maximum  $2\theta$  tolerance of 0.10. Input for the computer runs consisted of approximate cell parameters and observed  $2\theta$  values. The cell parameters were estimated by solving a system of equations simultaneously, each equation being generated from the formula.

$$\frac{1}{d^2(hkl)} = \frac{\frac{h^2}{a^2} + \frac{k^2}{c^2} - \frac{2hk}{ac} \cos \beta}{\sin^2 \beta} + \frac{l^2}{b^2}$$

The  $hkl$  values must be correct or an anomalous solution will occur. Usually there are enough diffraction lines present to set up more than one set of equations. Comparison between the sets then determines if the proper reflection planes have been chosen and, if so, the initial cell parameters to be used for input.

#### IV. DISCUSSIONS

##### A. Urea

Most materials are known to contract with decreasing temperature. Such an effect observed in the tetragonal unit cell of urea by Skaler et al. indicates that both dimensions decrease at a decreasing rate with temperature (Ref 4). They concluded that the intramolecular parameters were essentially unaffected within the error limits of the study, but the hydrogen bonds contracted. Urea has two distinct N-H...O bonds, one essentially parallel to the a direction and the other essentially parallel to the c axis. Both bonds are about 3.0 $\text{\AA}$  nitrogen to oxygen distance at room temperature. Upon cooling, the bond in the a direction contracts about 2% and the bond in the c direction contracts about 1%. Unfortunately, the study by Sklar et al. using x-rays, did not resolve the proton positions, so it was not possible to follow the temperature dependence of the proton positions or the N-H...O angles. The present work essentially confirms the results of the earlier study.

##### B. The Carbohydrates

Since low temperature unit cell parameters were obtained in only three of the carbohydrate cases attempted, there is rather limited data available for quantitative interpretations as originally intended. The available data is sufficient, however, for some qualitative observations. Of the nine axial contractions observed, eight fall within the range defined by the urea standard and the ninth exceeds this range only by .01 $\text{\AA}$ . The contractions are more or less isotropic and the exceptions to this rule are reasonable in terms of the known hydrogen bonding pattern of the crystals. The unit cell parameters at both temperatures as well as relative and absolute changes are shown in Table XII.

##### C. Sucrose

Sucrose has cell axes of roughly equal length and a roughly isotropic network of hydrogen bonds (Ref 7). The observed contraction is roughly isotropic in both absolute and relative terms. All three contractions fall into the urea range.

#### D. $\alpha$ -n-Acetyl-D-Glucosamine

This sugar shows contractions which are nearly isotropic in absolute terms, but with a relative contraction in the B direction about double that in the other two directions (Ref 5). Upon examination of the structure, it is found that the hydrogen bonding pattern projects about 2.0 hydrogen bond units on each axis. Thus the absolute contractions reflect the isotropic hydrogen bonding and the greater relative contraction in the B direction reflects the packing of the rings in the AC plane. It might also be mentioned however, that the hydrogen bonding in the B direction is in the form of infinite chains, while the bonding in the other two directions is in the form of single unit hydrogen bonds.

#### E. Celllobiose

Cellot<sup>+++</sup> shows contractions more or less similar to the other two sugars in the B and C directions but significantly less in the A direction (Ref 6). This is fairly consistent with the known hydrogen bonding pattern, since of the eight hydrogen bonds per unit cell, only one, the O (4) - O (2') has a major projection in this direction. The reason for the angular contraction is not obvious.

## V. CONCLUSIONS

While the low number of examples successfully investigated precludes this study from deciding the relative importance of hydrogen bond contractions and molecular geometry changes in producing unit cell contractions, it still has some value. In particular, the three new results do not contradict the model of Sklar *et al.* assigning the entire unit cell shrinkage to hydrogen bond contraction (Ref 4). This model then should be retained for comparison to infrared data, at least until more extensive x-ray data is available.

TABLE I X-RAY DATA FOR UREA

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	d $\text{\AA}$	<u>Intensity*</u>	<u>2θ</u>	d $\text{\AA}$	<u>Intensity*</u>
22.31	3.985	4200	22.60	3.934	4400
24.6 <sup>-</sup>	3.609	260	24.88	3.579	280
29.39	3.039	450	29.66	3.012	580
31.74	2.819	220	32.20	2.780	190
35.59	2.522	410	36.10	2.488	450
37.20	2.41 <sup>-</sup>	150	37.64	2.390	160
40.60	2.222	70	41.10	2.196	80
41.68	2.167	50	41.90	2.156	50

\* All intensity values are in counts per second.

TABLE II X-RAY DATA FOR SUCROSE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	d $\text{\AA}$	<u>Intensity*</u>	<u>2θ</u>	d $\text{\AA}$	<u>Intensity*</u>
11.71	7.557	150	11.78	7.512	120
12.78**	6.927	110			
12.89**	6.868	110	12.89	6.873	80
13.18	6.717	130	13.26	6.677	150
15.50	5.717	60	15.61	5.677	70
16.75	5.293	30			
18.88	4.700	250	19.02	4.666	250
19.62	4.524	200	19.75	4.495	180
20.40	4.353	90	20.52	4.328	50
20.88	4.254	50	21.00	4.226	70
22.08	4.026	70	22.24	3.997	80
22.54	3.944	30			
23.55	3.776	50	23.75	3.746	50
24.80	3.590	310	24.99	3.563	250
25.24	3.528	150	25.41	3.505	140
26.50	3.363	30	26.72	3.336	30
27.41	3.254	30	27.62	3.230	30
28.64	3.117	30			
31.02	2.883	50			

\* All intensity values are in counts per second.

\*\* Appears to be two peaks.

TABLE III X-RAY DATA FOR  $\beta$ -CELLOBIOSE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>	<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>
10.49	8.433	300	10.54	8.393	300
13.53	6.544	30	13.60	6.511	30
17.52	5.062	90	17.56	5.050	80
18.70	4.740	320	18.83	4.712	280
20.27	4.381	720	20.47	4.338	700
22.12	4.018	130	22.30	3.986	140
23.64	3.765	140	23.81	3.737	110
24.62	3.616	110	24.82	3.587	120
25.26	3.526	30	25.34	3.515	40
27.34	3.262	90	27.54	3.239	80
30.64	2.918	70	30.86	2.897	80

\* All intensity values are in counts per second.

TABLE IV X-RAY DATA FOR  $\alpha$ -n-ACETYL-GLUCOSAMINE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>	<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>
15.52	5.709	200	15.62	5.673	160
16.00	5.539	50	16.18	5.478	40
17.14	5.173	120	17.25	5.140	120
18.28	4.853	90	18.54	4.786	90
19.99	4.442	200	20.26	4.383	210
20.26	4.383	220	20.45	4.343	240
20.89	4.252	330	21.14	4.202	300
23.71	3.752	40			
24.47	3.638	30			
24.80	3.590	30			
25.24	3.528	30			
25.60	3.480	40			
25.94	3.435	40			
27.28	3.269	30			
27.75	3.215	430	28.17	3.168	440
30.15	2.964	90	30.50	2.931	80
30.92	2.892	120	31.42	2.847	200
31.40	2.849	240	31.54	2.836	250
32.04	2.793	10	32.18	2.782	60
34.68	2.586	10	34.98	2.565	40
36.62	2.455	30	36.79	2.443	40
37.10	2.423	70	37.54	2.396	60

\* All intensity values are in counts per second.

TABLE V X-RAY DATA FOR  $\alpha$ -D-GLUCOSE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u><math>2\theta</math></u>	<u>d<math>\text{\AA}</math></u>	<u>Intensity*</u>	<u><math>2\theta</math></u>	<u>d<math>\text{\AA}</math></u>	<u>Intensity*</u>
12.88**	6.874	150			
14.75	6.006	100			
17.70	5.011	50			
18.60	4.770	100			
18.88	4.700	90			
19.90	4.461	550	20.02	4.435	600
20.36	4.362	440	20.49	4.335	470
20.72	4.289	490	20.86	4.258	490
21.81	4.073	50	21.95	4.049	50
22.96	3.866	210	23.08	3.852	300
23.64	3.764	30			
24.80	3.590	10			
25.61	3.478	170	25.76	3.458	170
26.74	3.334	60	26.90	3.314	60
27.80	3.209	80	27.96	3.190	90
28.52	3.129	300	28.65	3.116	300
29.59	3.020	60	29.66	3.012	50
30.85	2.898	30			
31.38	2.850	100			

\* All intensity values are in counts per second.

\*\* Possibly two peaks.

TABLE VI X-RAY DATA FOR  $\beta$ -D-GLUCOSE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>	<u>2θ</u>	<u>dÅ</u>	<u>Intensity</u>
16.50	5.372	320	16.69	5.311	260
17.07	5.194	380	17.10	5.185	340
17.92	4.950	70	18.08	4.905	90
19.34	4.589	500	19.75**	4.495	410
20.60	4.311	350	20.95	4.240	280
21.70	4.096	90	21.80	4.077	120
23.54	3.780	500	23.94**	3.715	400
24.60	3.619	240	24.95	3.569	200
26.90	3.314	140	26.95	3.308	120
28.30	3.154	160	28.07	3.178	170
28.56	3.128	100	28.84	3.094	90
31.40	2.849	60			
31.85	2.810	180	32.06	2.791	180
32.92	2.720	70			

\* All intensity values are in counts per second.

\*\* Peak considerably broader than room temperature run and considerable decrease in intensity.

TABLE VII X-RAY DATA FOR RAFFINOSE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>	<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>
12.49**	7.087	190	12.55***	7.053	240
12.91	6.857	150	12.99	6.814	30
13.31	6.652	230	13.47	6.574	60
14.46**	6.125	130	14.51	6.104	70
16.28**	5.445	80	16.48**	5.378	50
16.66**	5.321	100	16.80	5.277	80
17.98	4.934	80	18.10	4.901	50
19.42**	4.570	130	19.50	4.552	80
20.25	4.385	30	20.55	4.322	50
20.82	4.266	380	20.92**	4.246	160
22.44	3.962	60	22.55	3.943	30
22.94**	3.876	100	23.04	3.859	60
23.52	3.782	220	23.67	3.759	60
24.68**	3.607	60			
24.96	3.567	50	25.14	3.542	20
25.69	3.467	160	25.94**	3.434	70
26.40	3.376	60	26.58	3.353	30
28.35	3.148	60	28.45	3.137	30
29.01	3.078	70	29.19	3.059	30
30.52	2.929	30			
31.12	2.874	80	31.32	2.855	50

\* All intensity values are in counts per second.

\*\* Possibly two peaks.

\*\*\* Considerable increase in intensity and sharpening of peak.

TABLE VIII X-RAY DATA FOR MALTOSA

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>	<u>2θ</u>	<u>dÅ</u>	<u>Intensity*</u>
14.43	6.137	170	14.48	6.116	170
18.39	4.824	70	18.58**	4.788	50
19.28	4.604	180	19.50	4.552	150
20.15	4.407	220	20.35	4.364	220
21.14	4.202	120	21.34	4.163	100
21.92	4.054	260	22.11	4.020	250
23.62	3.767	50	23.75	3.746	40
24.21	3.676	50	24.50	3.633	40
25.16	3.540	50	25.29	3.521	40
26.22	3.400	80	26.44	3.370	80
27.82	3.206	40	28.00	3.186	30
29.04	3.075	40	29.25	3.053	30
30.03	2.976	40	30.28	2.952	30
30.92	2.892	40	31.08	2.877	30
31.81	2.813	50	32.05	2.792	40

\* All intensity values are in counts per second.

\*\* Peak somewhat broader than Room Temperature run.

TABLE IX X-RAY DATA FOR ARABINOSE

ROOM TEMPERATURE			LIQUID NITROGEN TEMPERATURE		
<u>2θ</u>	d $\text{\AA}$	<u>Intensity*</u>	<u>2θ</u>	d $\text{\AA}$	<u>Intensity*</u>
14.30	6.194	420	14.52**	6.100	300
16.33	5.426	420	16.53**	5.362	260
18.24	4.864	70	18.26	4.858	70
20.45	4.343	560	20.74**	4.283	440
22.86	3.889	300	23.20	3.834	210
23.30	3.818	50	23.66	3.760	70
24.64	3.612	50	24.98	3.564	40
27.37	3.260	120	27.76	3.216	100
27.73	3.216	440	28.14	3.171	360
28.86	3.093	60	29.28	3.050	40
29.41	3.037	70	29.68	3.010	70
33.08	2.708	320	33.43	2.680	300

\* All intensity values are in counts per second.

\*\* Peak somewhat broader than room temperature run and considerable decrease in intensity.

TABLE X UNIT CELL REFINEMENTS AT ROOM AND LIQUID NITROGEN TEMPERATURES

	<u>a</u>	<u>b</u>	<u>c</u>	<u><math>\beta</math></u>
<b>UREA</b>				
Room Temperature	5.64		4.70	
Liquid Nitrogen Temperature	5.56		4.68	
<b>SUCROSE</b>				
Room Temperature	10.86	8.71	7.76	102.9°
Liquid Nitrogen Temperature	10.79	8.65	7.70	103.0°
<b>CELLOBIOSE</b>				
Room Temperature	10.98	13.11	5.09	90.9°
Liquid N <sup>2</sup> o <sub>2</sub> Temperature	10.96	13.02	5.05	89.4°
<b><math>\alpha</math>-n-ACETYL-GLUCOSAMINE</b>				
Room Temperature	11.27	4.84	9.71	113.6°
Liquid Nitrogen Temperature	11.20	4.78	9.66	113.7°

TABLE XI UNIT CELL PARAMETERS  
OF VARIOUS SUGARS AT ROOM TEMPERATURE

<u>COMPOUND</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u><math>\beta</math></u>	<u>Ref</u>
Urea	5.662	----	4.716	----	1
Sucrose	10.89	8.69	7.77	103.0°	4
$\beta$ -Cellobiose	10.94	13.05	5.11	90.0°	3
$\alpha$ -D-acetyl-glucosamine	11.25	4.82	9.72	113.7°	2
$\alpha$ -D-glucose	10.36	14.84	4.97	----	8
$\beta$ -D-glucose	9.29	12.65	6.70	----	5
Raffinose	8.966	12.327	23.837	----	6
Maltose	4.92	15.23	10.68	97.53°	9
$\beta$ -Arabinose	5.925	7.820	13.354	99.45°	7

TABLE XII

## Results: Low Temperature X-Ray Diffraction Simple Sugars

	300°K	100°K	Ratio	Δ%	Δ
$\alpha$ -n-Acetyl-D-Glucosamine					
a	11.27	11.20	.9938	.32	.07 $\text{\AA}$
B	4.84	4.78	.9876	1.24	.06 $\text{\AA}$
C	7.76	7.70	.9948	.52	.05 $\text{\AA}$
$\beta$	113.60	113.70	.9991	.09	.1°
Sucrose					
a	10.86	10.79	.9936	.64	.07 $\text{\AA}$
B	8.71	8.65	.9931	.69	.06 $\text{\AA}$
C	7.76	7.70	.9923	.77	.06 $\text{\AA}$
$\beta$	102.9	103.0	.9990	.1	.1°
$\beta$ -Cellulose					
a	10.98	10.96	.9982	.18	.02 $\text{\AA}$
B	13.11	13.02	.9931	.69	.09 $\text{\AA}$
C	5.09	5.05	.9921	.78	.04 $\text{\AA}$
$\beta$	90.9 °	89.4 °	.9835	1.65	1.3 °
Urea					
a	5.64	5.56	.9858	1.42	.08 $\text{\AA}$
B					
C	4.70	4.68	.9957	.43	.02 $\text{\AA}$

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